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EXECUTIVE SUMMARY

A SIMPLE MODEL FOR THE EVOLUTION OF THE T_2 PROFILE IN SOIL EXPOSED TO AN ATMOSPHERE CONTAINING T_2

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A process of major importance to determining the impact of a release of molecular tritium gas, T_2, is the uptake and conversion of T_2 to the much more radiotoxic form of tritiated water, HTO, by surface soils. For the purpose of modelling the fate and impact of a T_2 release, this process may be parameterized by a deposition velocity. An ongoing research program, involving both theoretical and experimental studies of this process, is underway.

A simple, theoretical model was developed previously to describe the steady-state depth profile of molecular tritium in soil exposed to an atmosphere containing a constant concentration of T_2. This report describes an extension of that model to deal with the time evolution of the T_2 profile. It is shown that the time varying T_2 profile leads to a T_2 uptake rate (and hence apparent T_2 deposition velocity) that also varies with time until steady state is reached. The implications for deposition velocity measurements using chamber techniques are investigated and it is concluded that, provided certain constraints are met, measured deposition velocities should closely approximate steady-state values.

G.O.

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740635-503-091	837.262	October 11, 1984	84-260-K

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To Mr. F.J. Kee
Director of Research

A SIMPLE MODEL FOR THE EVOLUTION OF THE T_2 PROFILE IN SOIL EXPOSED TO AN ATMOSPHERE CONTAINING T_2

G. Ogram

ABSTRACT

A model developed previously for the deposition velocity, v_g, of molecular tritium (T_2) to soil is extended to describe the time evolution of the T_2 profile within the soil. The implications for experimental measurements of v_g are discussed and it is concluded that, provided certain conditions are met, chamber experiments should give representative values of v_g.

1.0 INTRODUCTION

A previous report (Ogram, 1982) described a simple model for the steady-state depth profile of molecular tritium gas, T_2, in a sample of soil exposed to an atmosphere containing a constant concentration of T_2. The model was used to derive an expression for deposition velocity. That treatment is extended here to deal with the question of how quickly the steady state profile is approached. This will be shown to have implications for measurements of T_2 deposition rates carried out using exposure chambers in the environment.

Interest in the problem of T_2 deposition to soil arises because of the importance of in-soil processes which convert molecular tritium to the much more radiotoxic form HTO. Under a range of environmental conditions, this is expected to be the dominant process responsible for converting tropospheric T_2 to HTO (Ogram, 1982). Dry deposition due to uptake by soils will also largely determine the rate of depletion, and hence the travel distance of a plume of released T_2.

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For modelling the fate of an atmospheric plume of T_2, it is convenient to use the concept of a deposition velocity, v_g, to parameterize the rate of disappearance of T_2 from the air due to conversion within the soil.

The flux J of T_2 to the soil can thereby be written as

$$J = N_o v_g \tag{1}$$

where N_o is the concentration of T_2 in the atmosphere above the soil surface.

In the following, a model is developed which describes the evolution of the T_2 profile within the upper soil layer on exposure to a constant T_2 concentration, beginning at some instant in time. An expression for v_g is derived and the implications for experimental measurements of v_g are then briefly discussed.

2.0 MODEL

The problem is shown conceptually in Figure 1. Following time t = 0, an area A of soil is exposed to an atmosphere containing a constant concentration N_o of T_2. T_2 diffuses into the soil where it is converted to HTO. The following assumptions are made:

- Soil properties are homogeneous. That is, the effective diffusion coefficient for T_2, and the local rate coefficient of conversion of T_2 to HTO are independent of soil depth, z, over the depth of significant penetration of T_2 into the soil.

- The rate of conversion is first order in tritium concentration. (At the very low concentrations likely in the environmental situation, second order effects, such as radiation-induced chemistry are unlikely).

- The resistance to surface uptake is the rate limiting step for T_2 deposition to soils. (The deposition velocity v_g can be written as $v_g = (r_s + r_a)^{-1}$ where r_s is the resistance to uptake at the surface and r_a is the resistance to atmospheric transfer, including resistance to turbulent transport and resistance to diffusive transport through the surface sublayer (eg, Wesely and Hicks, 1977)). If uptake is rate limiting then $v_g \approx r_s^{-1}$. Typically $r_a^{-1} \sim 1$ cm s^{-1} whereas for T_2 deposition $v_g \lesssim 0.1$ cm s^{-1}, as discussed later in Section 3. This assumption, therefore, appears reasonable for most conditions.

The following continuity equation then describes the evolution of the T_2 concentration profile, N(z,t) within the soil.

$$\frac{\partial N(z,t)}{\partial t} = D \frac{\partial^2 N(z,t)}{\partial z^2} - kN(z,t) \tag{2}$$

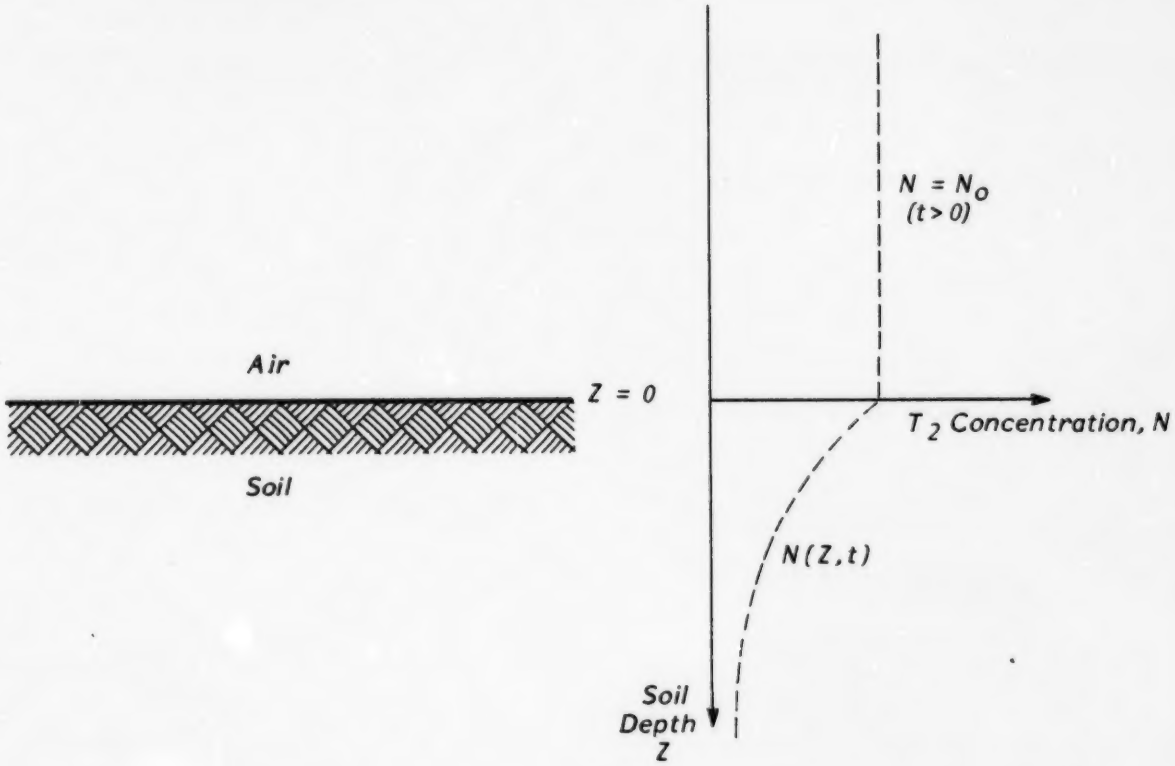

FIGURE 1

CONCEPTUAL SKETCH OF THE SITUATION ANALYSED IN THE TEXT OF AN AREA OF SOIL EXPOSED TO AN ATMOSPHERE CONTAINING T_2

where D is the diffusion coefficient for T_2 gas in the soil and k is the rate coefficient for conversion of T_2 to H_2O. The boundary conditions are

$$N(z,o) = 0 \text{ for } z > 0 \tag{3a}$$

$$N(o,t) = N_o \text{ for } t \geq 0 \tag{3b}$$

For convenience, the convention used is that z is zero at the soil surface and positive in the downwards direction.

These equations are solved in Appendix 1 by a Laplace transform method to give

$$\frac{N(z,t)}{N_o} = \exp(-z/z_e) + \frac{1}{2}\left[\exp(z/z_e)\left\{1 - \operatorname{erf}\left(\sqrt{kt} + \frac{z}{2\sqrt{Dt}}\right)\right\} - \exp(-z/z_e)\left\{1 - \operatorname{erf}\left(\sqrt{kt} - \frac{z}{2\sqrt{Dt}}\right)\right\}\right] \tag{4}$$

where $z_e = \sqrt{D/k}$.

As t increases this expression approaches the steady state profile derived previously (Ogram, 1982).

$$N(z) = N_o \exp(-z/z_e) \tag{5}$$

At steady state, the concentration profile decreases exponentially with a scale depth of ze. This steady state is characterized by the amount of T_2 passing into the soil per unit time being balanced by the amount of T_2 converted per unit time within the soil.

It is useful to write the above equations in non-dimensional form. Equations (4) and (5) become, respectively.

$$n(\delta,\tau) = e^{-\delta} + \frac{1}{2}\left[e^{\delta}\left\{1 - \operatorname{erf}(\sqrt{\tau} + \delta/2\sqrt{\tau})\right\} - e^{-\delta}\left\{1 - \operatorname{erf}(\sqrt{\tau} - \delta/2\sqrt{\tau})\right\}\right] \tag{4a}$$

and

$$n(\delta) = e^{-\delta} \tag{5a}$$

where $\delta = z/z_e$ is the non-dimensional depth, $\tau = tD/z_e^2$ is the non-dimensional time and $n = N/N_o$ is the normalized T_2 concentration.

Figure 2 shows n plotted against δ for various values of τ.

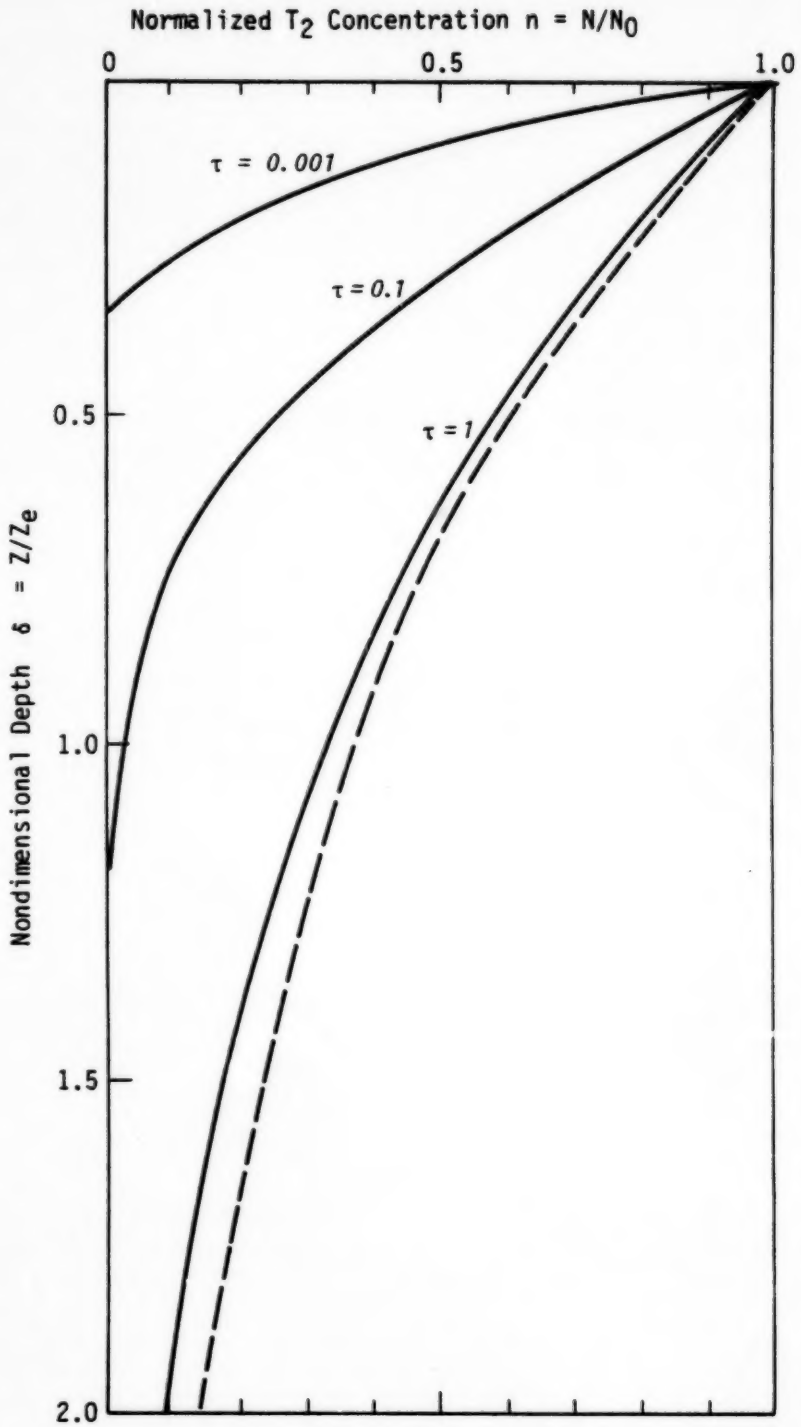

FIGURE 2

NORMALIZED T_2 CONCENTRATION PROFILES CALCULATED FOR VARIOUS NONDIMENSIONAL TIMES τ. THE DASHED LINE SHOWS THE STEADY STATE PROFILE ATTAINED AS τ BECOMES LARGE.

If the flux of T_2 into the soil is due to diffusion alone, the magnitude of the flux at the soil surface is given by Fick's Law.

$$J(t) = - D \nabla N (z,t) \Big|_{z \to o} \tag{6}$$

From equation (1)

$$v_g = J/N_o = D\nabla N/N_o \Big|_{z \to o} \tag{7}$$

Note that for a fixed value of D, v_g depends on the gradient of the normalized profile alone which according to (4) varies with time until steady state conditions are reached.

Using equations (4) and (6) the following expression can be derived for an effective deposition velocity

$$v_g(t) = \sqrt{kD} \quad [2 - \text{erf} \ (\sqrt{kt})] \quad + \quad \sqrt{D/\pi t} \quad \exp \ (-kt) \tag{8}$$

which as t becomes large approaches the steady state value

$$v_{g\infty} = \sqrt{kD} \tag{9}$$

As $\sqrt{D/k} = z_e$, (9) may also be written as $v_{g\infty} = kz_e = D/z_e$.

Expressed in non-dimensional form equation (7) becomes

$$\nu(\tau) = [\, 2 - \text{erf} \ (\sqrt{\tau}) + (1/\sqrt{\pi\tau}\,) \ e^{-\tau}] \tag{8a}$$

where $\nu(\tau) = v_g/v_{g\infty}$.

Figure 3 shows a plot of non-dimensional deposition velocity ν against non-dimensional time τ (equation 8a).

3.0 DISCUSSION

Because the model involves some simplifying assumptions (eg, uniform reactivity and diffusivity) it is likely only to approximate what actually occurs in a "real" environment. However, the model may provide a useful framework both for the design of experiments to measure v_g and its dependence on environmental factors, and for the interpretation of experimental results. Some implications of the model results are discussed below.

Figures 2 and 3 show that while a profile of steady state form (equation 5) is being established, the normalized T_2 profile, and hence the apparent deposition velocity are time varying.

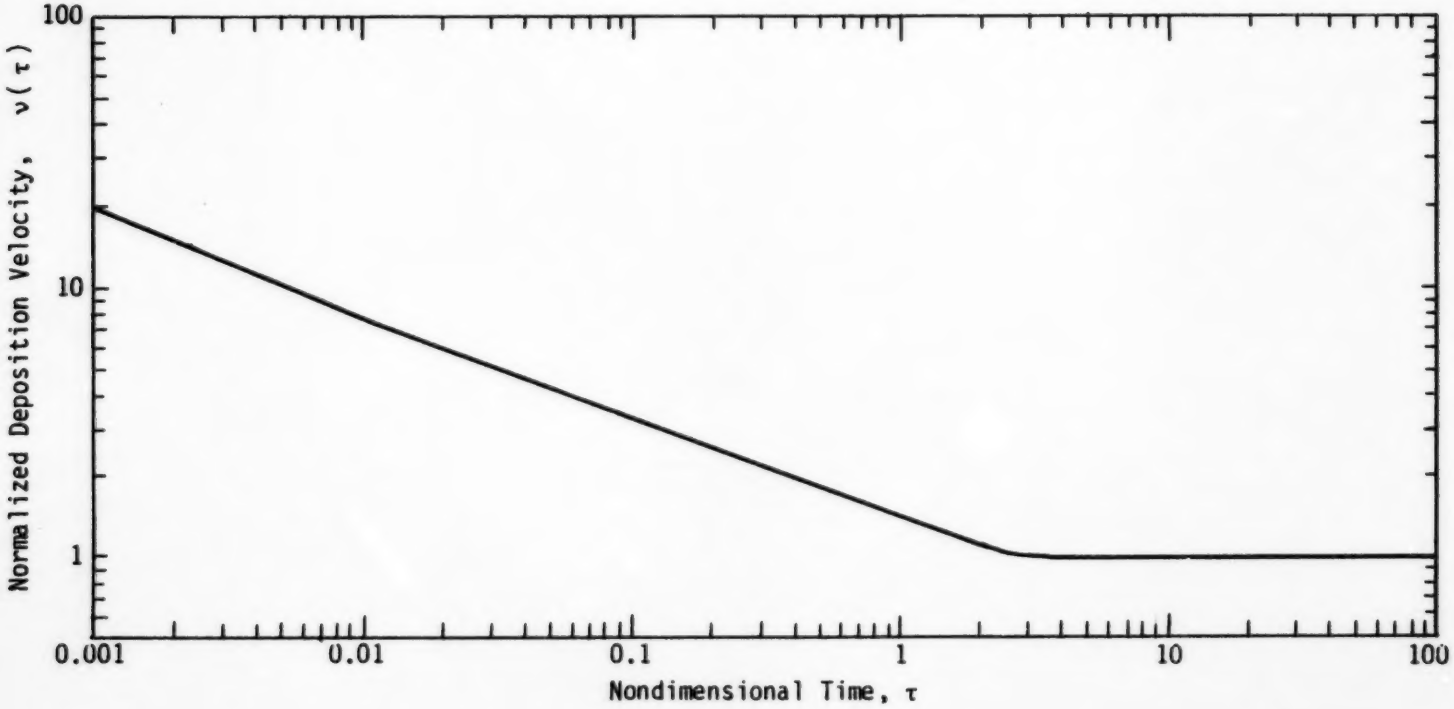

FIGURE 3

PLOT OF NONDIMENSIONAL DEPOSITION VELOCITY $v = v_g/v_{g_\infty}$ AGAINST NONDIMENSIONAL TIME $\tau = tD/Z_e^2$. $v = 1$ IS THE STEADY STATE VALUE APPROACHED AS τ BECOMES LARGE.

Measurements of v_g have been carried out using two methods: (i) by measuring the amount of HTO accumulated in soil exposed, for a known time period, to air containing a constant concentration of T_2; (ii) by measuring the rate of decay of T_2 concentration in the air of a sealed chamber used to isolate an area of soil.

Method (i) corresponds directly to the situation analyzed here. In this case the total tritium deposited as HTO to the soil is given by

$$\int_{t = 0}^{t = t^1} A\, v_g(t)\, N_o\, dt$$

where t^1 is the duration of the experiment.

Figures 2 and 3 show that to get representative v_g's, t^1 should be such that the corresponding non-dimensional time $\tau^1 = t^1\, D/z_e^2$ is much greater than unity. If $t^1 >> 1$ then the experimentally determined v_g will closely approximate the steady state value, $v_{g\infty}$, because the total tritium deposited $\int_o^{t^1} A\, v_g(t)\, N_o dt$ is approximately equal to $A\, v_{g\infty}\, N_o t^1$. The time scales involved for typical experimental conditions will be estimated later in this Section, as we need to first discuss the application of the model to experiments of type (ii).

The present model does not strictly apply to method (ii) as the concentration of T_2 in the chamber air, N_o, decreases with time. However, if the experimental design is such that the time constant, t_v, for the decay of N_o is much longer than the time, t_{ss}, taken to achieve a steady state profile (ie, $t_v >> t_{ss}$), then the concentration profile in the soil, normalized to the instantaneous value of N_o, will have a form that is close to the steady state profile (equation 5). That is, the local T_2 concentrations, $N(z,t)$, will decrease as N_o decreases, but the normalized concentration profile should be approximately invariant in time, as the profile will have sufficient time to follow changes in air concentration, N_o. The deposition velocity measured should thus give a value that is constant in time, independent of N_o, and close to the asymptotic value $v_{g\infty}$.

It can be readily shown that $t_v = V/Av_g$, (eg, Ogram, 1982) where V is the chamber volume. Usually, V/A is the chamber height h. The criterion $t_v/t_{ss} = h/v_g\, t_{ss} >> 1$ can thus be satisfied by making h sufficiently large (as v_g and t_{ss} are, of course, independent of h). It will be shown later that this criterion apprears to have been met in past measurements of v_g using method (ii).

An idea of the actual time scales involved in the approach to steady state may be estimated using available experimental data. We may define the time, t_{ss}, taken to achieve an approximate steady state profile as the time at which $v_g(t) = 1.1\, v_{g\infty}$ (ie, $\nu(\tau_{ss}) = 1.1$). From Figure 3 we see that $\tau_{ss} \simeq 2$.

We now note that $t_{ss} = \tau_{ss} z_e^2/D$, can also be written as $t_{ss} = \tau_{ss} z_e/v_{g\infty}$ using the relations given in Section 2.0. Both z_e and v_g values have been experimentally measured. Making the assumption that measured v_g values represent $v_{g\infty}$ reasonably well we can derive values for t_{ss}. We will ultimately show that this assumption is justified.

Various experiments (Garland and Cox, 1980; Sweet and Murphy, 1982; Ogram, 1984) indicate v_g values in the range 0.001 to 0.1 cm s^{-1}. It remains to estimate z_e. In some of the above experiments, profiles of deposited HTO were also measured by analyzing vertically segmented soil cores. We assume that the measured normalized profiles of HTO approximate the steady state T_2 profiles in these cases, hence z_e can be estimated from the slope of a semilogarithmic plot of the depth profile using equation (5). This assumption would be valid if: the normalized T_2 profile had approximate steady state form for much of the duration of the experiment (ie, $t \gg t_{ss}$ and in the case of method (ii), $t_v/t_{ss} \gg 1$); D and k did not vary greatly over a depth of about z_e; and subsequent diffusion or evaporation of HTO did not significantly distort the profile before samples were taken. The last condition is likely to hold if the samples were taken immediately upon completion of an experiment. The diffusion coefficient for HTO in soil is very small ($\sim 10^{-5}$ cm^2 s^{-1}, Garland, 1980) as most of the HTO is present in the soil in the liquid phase. The time taken for an initial pulse of HTO at a particular depth to diffuse to a distribution having a vertical standard deviation of σ_z is $t_{dif} = \sigma_z^2/D$. For $\sigma_z = 1$ cm the corresponding value of t_{dif} is 28 h, which is much longer than a typical experimental duration of a few hours. If cores are taken and segmented immediately after an experiment, then profile features should be resolvable on a scale of less than 1 cm.

Typical z_e values appear to be in the range of 0.5 to 5 cm. A range of values of t_{ss} corresponding to $\tau_{ss} = 2$ can be calculated and are shown in Table Ia for various values of v_g and z_e.

For comparison values of t_v ($=h/v_g$) are shown in Table Ib for h = 10 and 100 cm. In general $t_v \gg t_{ss}$, particularly for h = 100 cm. Thus an experimental chamber with h $\sim$100 cm (eg, Sweet and Murphy, 1982; Ogram, 1984) should give meaningful v_g values. (This may also be demonstrated by observing that $\tau_v = t_v D/z_e^2 = (h/v_g)(v_g/z_e)$ and if $t_v \gg t_{ss}$, $v_g \rightarrow v_{g\infty}$ so $\tau_v = h/z_e$. The criterion $t_v \gg t_{ss}$ can thus be written $\tau_v = h/z_e \gg 2$ which certainly holds for the range of values of z_e given above if h $\sim$100 cm).

In many cases the soil factors affecting v_g and z_e (ie, k and D) may be, to a good approximation, constant over the range of penetration of T_2 into the soil (which, of course, is $\sim z_e$) and the present theory might apply reasonably well. However, under certain conditions, such as after a recent rainfall, D and k, may show a significant variation within a few cm depth. D may also vary if soil particle sizing and packing change with depth. The model could be extended to deal with these cases, if the form of the profiles of

TABLE I

(a) t_{ss}, TIME TO REACH STEADY STATE T_2 PROFILE (IN SECONDS), FOR VARIOUS DEPOSITION VELOCITIES, v_g, AND SCALING LENGTHS, z_e

v_g (cm s^{-1}) \ z_e (cm)	0.5	5
0.1	10	100
0.01	100	1 000
0.001	1 000	10 000

(b) t_v THE TIME CONSTANT (IN SECONDS) FOR DECAY OF T_2 CONCENTRATION IN A CHAMBER EXPERIMENT (WITH CHAMBER HEIGHT h)

v_g (cm s^{-1}) \ h (cm)	10	100
0.1	100	1 000
0.01	1 000	10 000
0.01	10 000	100 000

k and D were known, by allowing k and D in equation (2) to be depth dependent. However, in this case, equation (2) would probably have to be solved numerically.

It should be possible to test the validity of this model using soil samples in the field and the laboratory. This could be done by making simultaneous measurements of v_g, z_e and D (including its variation with depth over the range of interest, ie, $z < \sim 10$ cm).

The model developed here may have implications for the effective deposition velocities experienced by a puff or plume of released T_2. The problem is beyond the scope of the present treatment as the concentrations of T_2 to which the soil is exposed can vary in a complicated way with time. As the puff or plume traverses an area of soil the T_2 concentrations in the soil will increase. However, after passage of the puff or plume some of the T_2 in the soil will tend to diffuse back into the atmosphere. Equation (2) can be solved with an appropriate time varying boundary condition to investigate the effect of the consequent time variation of T_2 soil profiles on conversion and depletion rates. Again, transient effects are unlikely to be significant if the time scale for variation of puff or plume concentration at any point is much longer than the time taken to reach an approximate steady state T_2 profile in the exposed soil.

4.0 CONCLUDING REMARKS

A previously-developed model for the deposition velocity of elemental tritium to soil was extended to obtain an expression for the time taken to achieve a steady state T_2 profile in the soil. This steady state is achieved when the rate at which T_2 enters the soil is balanced by the rate at which T_2 is converted to HTO within the soil and may be characterized by a constant deposition velocity.

The expression derived for the depth profile of T_2 concentration, and for deposition velocity were expressed in non-dimensional form which allows the results to be scaled to apply to a wide range of soil parameters.

The implications of these results for experimental methods of measuring deposition velocities were investigated, and it was concluded that in most cases the normalized concentration profile of T_2 in the soil achieves and maintains a steady state rapidly enough for transient effects to have little impact on inferred deposition velocities.

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APPENDIX I

DERIVATION OF T_2 PROFILE
(Equation 4 in text)

The continuity equation, (equation 2 in text) is

$$\frac{\partial N(z,t)}{\partial t} = D \frac{\partial^2 N}{\partial z^2} - kN \qquad \text{(A1)}$$

with boundary conditions

$$N(z,o) = O \qquad z > O \qquad \text{(A2)}$$

$$N(o,t) = N_O \qquad t \geq O \qquad \text{(A3)}$$

D and k are taken to be constants, independent of depth z.

The Laplace transform of (A1) with respect to t is

$$sF - N(z,o) = D \frac{\partial^2 F}{\partial z^2} - kF \qquad \text{(A4)}$$

where $F(x,s) = \int_o^\infty e^{-st} N(z,t)\, dt$.

Using (A2) and rearranging, (A4) becomes

$$\frac{\partial^2 F}{\partial z^2} - \left(\frac{k+s}{D}\right) F = O \qquad \text{(A5)}$$

which has the solution

$$F = \frac{N_O}{S} \exp\left[-\left(\frac{k+s}{D}\right)^{1/2} z\right] \qquad \text{(A6)}$$

where the exponentially growing solution has been rejected as unphysical and the boundary condition

$$F(0,s) = N_O/s,$$

obtained by transforming (A3), has been used.

The T_2 profile, N(z,t), is given by the inverse transform of A(6), ie,

$$N(z,t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{N_O}{s} \exp\left[-\left(\frac{k+s}{D}\right)^{1/2} z\right] e^{st}\, ds \qquad \text{(A7)}$$

where c is real and >o.

This integral may be evaluated by using the contour, in the complex s plane, shown in Figure A1.

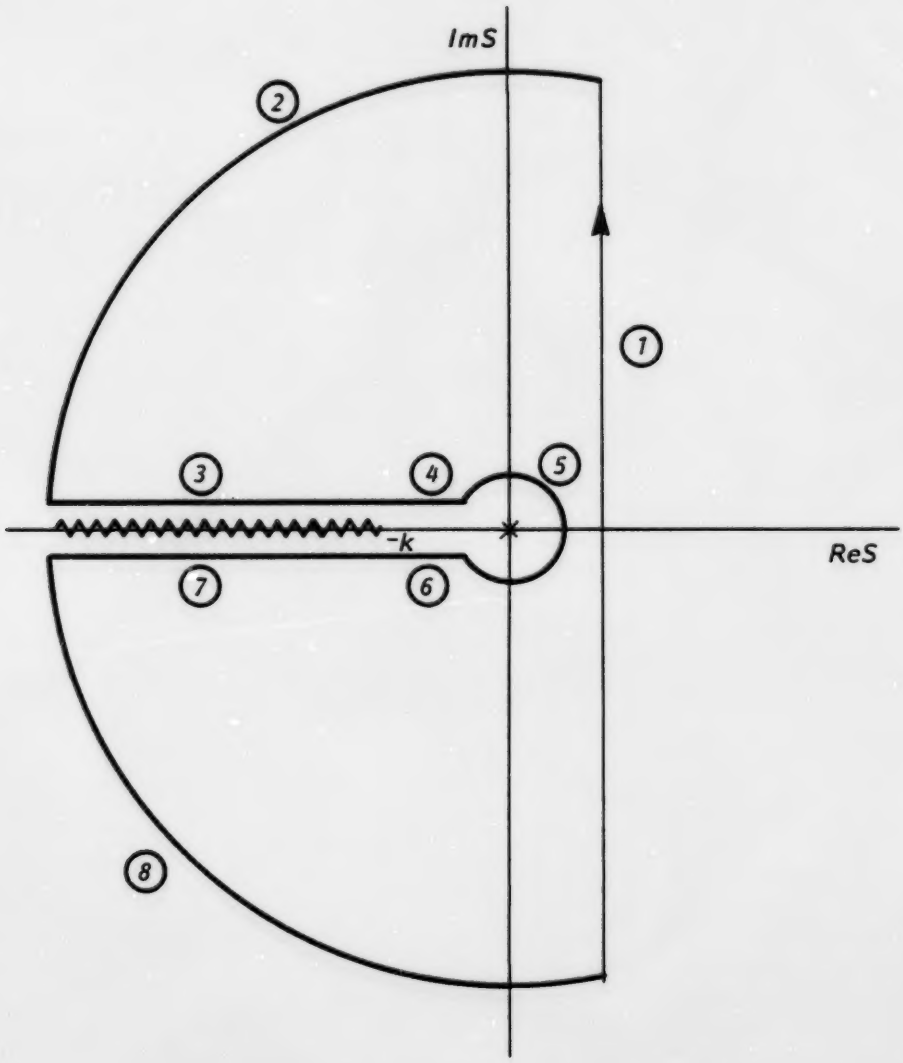

FIGURE A1

CONTOUR IN COMPLEX S PLANE FOR EVALUATION
OF INVERSE LAPLACE TRANSFORM (A7)

Note that s = o is a pole of order unity and s = -k is a branch point. A branch cut is chosen such that for S<-k, $\sqrt{(s+k)}$ has real and imaginary parts ≥o above the -ve s axis and an imaginary part ≤o below the -ve s axis. The contour contains no singularities so the integral around the contour is zero. If we denote the contribution to the integral along each part of the contour as numbered in Figure 1, then

$$N(z,t) = ① = -② - ③ - ④ - ⑤ - ⑥ - ⑦ - ⑧ \qquad \text{(A8)}$$

The contributions along ② and ⑧ can be shown to vanish as $|s| \to \infty$*.

Contributions ④ and ⑥ cancel.

The contribution around ⑤ can be evaluated by residues

$$⑤ = 2\pi i \left\{ -\frac{1}{2\pi i} N_o \exp\left[-\left(\frac{k}{D}\right)^{1/2} z\right] \right\} \qquad \text{(A9)}$$

$$③ = \frac{1}{2\pi i} \int_{-\infty}^{-k} \frac{N_o}{s} \exp\left[-\left(\frac{k+s}{D}\right)^{1/2} z\right] e^{st}\, ds.$$

Let u = k+s, then

$$③ = \frac{1}{2\pi i} \int_{-\infty}^{o} \frac{N_o}{u-k} \exp\left(-u^{1/2} D^{-1/2} z\right) e^{ut} e^{-kt}\, du$$

$$= \frac{-1}{2\pi i} \int_{o}^{-\infty} \frac{N_o}{u-k} \exp\left(-u^{1/2} D^{-1/2} z\right) e^{ut} e^{-kt}\, du$$

Now on branch chosen: u is -ve real and the square root of u is $+\sqrt{u}$, therefore $u^{1/2} = i\sqrt{(-u)}$.

therefore ③ becomes

$$-\frac{1}{2\pi i} \int_{o}^{\infty} \frac{N_o}{u-k} \exp\left[-i(-u)^{1/2} D^{-1/2} z\right] e^{ut} e^{-kt}\, du.$$

---

*This can be shown by observing that

$$\left| \frac{1}{s} \exp\left[-\left(\frac{k+s}{D}\right)^{1/2} z\right] e^{st} \right| \leq \left| \frac{e^{st}}{s} \right|$$

as $\left[\left(\frac{k+s}{D}\right)^{1/2} z\right]$ always has a real part ≥o on the arc. The integral of the right hand side of this inequality can be shown to vanish along a similar arc, thus the integral of the left hand side must also vanish. (The right hand side is the integrand for the inverse transform of f(z) = 1, z>o and appears in many standard texts, eg, Matthews and Walker, 1970.)

Changing the variable to $v = -u$ gives

$$③ = \frac{-1}{2\pi i} \int_o^\infty \frac{N_o}{v+k} \exp\left(-iv^{1/2} D^{-1/2} z\right) e^{-vt} e^{-kt} dv \qquad (A10)$$

Similarly,

$$⑦ = \frac{1}{2\pi i} \int_o^\infty \frac{N_o}{v+k} \exp\left(iv^{1/2} D^{-1/2} z\right) e^{-vt} e^{-kt} dv \qquad (A11)$$

Using the relationship

$$\sin x = (e^{ix} - e^{-ix})/2i$$

$$③ + ⑦ = \frac{1}{\pi} \int_o^\infty \frac{N_o}{v+k} e^{-vt} e^{-kt} \sin\left(v^{1/2} D^{-1/2} z\right) dv$$

let $x = v^{1/2}$, then

$$③ + ⑦ = \frac{2e^{-kt}}{\pi} \int_o^\infty \frac{N_o x}{x^2+k} e^{-x^2 t} \sin\left(x D^{-1/2} z\right) dx \qquad (A12)$$

This is a tabulated integral (Gradshteyn and Ryzik, 1965). Thus

$$③ + ⑦ = \frac{-N_o}{2} \left[2 \sinh\left(2\sqrt{k/D}\right) + \exp\left(-z\sqrt{k/D}\right) \operatorname{erf}\left(\sqrt{kt} - \frac{z}{2\sqrt{Dt}}\right) - \exp\left(z\sqrt{k/D}\right) \operatorname{erf}\left(\sqrt{kt} - \frac{z}{2\sqrt{Dt}}\right)\right] \qquad (A13)$$

Where $\operatorname{erf}(x) = (2/\pi^{1/2}) \int_o^x e^{-t^2} dt$ is the error function (Abramowitz and Stegun, 1965).

Therefore, from (A8), (A9) and (A13) we have

$$N(z,t)/N_o = \exp(-z/z_e) + \frac{1}{2}\left[\exp(z/z_e)\left\{1 - \operatorname{erf}\left(\sqrt{kt} + \frac{z}{2\sqrt{Dt}}\right)\right\} - \exp(-z/z_e)\left\{1 - \operatorname{erf}\left(\sqrt{kt} - \frac{z}{2\sqrt{Dt}}\right)\right\}\right] \qquad (A14)$$

where we have written $z_e = \sqrt{D/k}$ and used the relationship

$$\sinh(x) = (e^x - e^{-x})/2$$